Adsorption of Acid Dyes on Anionic Clays

by

Mohd Hakim Mohd Rashid

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

(Assoc. Prof. Dr. Ye Lwin)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD HAKIM MOHD RASHID

ABSTRACT

The presence of colour in many industrial effluent streams especially from the textile industry is aesthetically undesirable. Traditionally both biological and chemical methods have been employed for dye removal from waste streams, but these techniques have not been successful due to its highly structured polymers which are very difficult to decompose. Many physical and chemical treatment methods including coagulation, precipitation, filtration, membrane separation and oxidation have been used for the treatment of dye-containing effluents. Over the last few decades, sorption (as adsorption, biosorption and ion exchange) has gained importance as an effective purification and separation technique used in wastewater treatment. Activated carbon has been the most widely used adsorbent because of its high capacity for the adsorption of organic species. However due to the difficulty, high cost and expensive regenerationof the activated carbon, clays are being considered as alternative low cost adsorbents. A potential candidate is the hydrotalcite, a type of layered double hydroxide (LDH), occurs as natural clay like mineral and can be readily synthesized by co-precipitation method.

ACKNOWLEDGEMENT

I would like to take this opportunity to thank and express my gratitude to all the parties involved in assisting me to complete and accomplish this final year project. There were many obstacles that would have never been overcome without these individuals.

Firstly, I would like to convey my sincere gratitude to my final year project supervisor **Assoc. Prof. Dr. Ye Lwin @ Mohammed Hussein** for his continuous guidance and supervision which without him, this project would have never been able to initiated let alone is completed. His readiness to help me as one of his students is very commendable. Whenever we were in the dark, he always there to help.

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My deepest gratitude to the entire lab technician's involved aong the progress of my experimentation. Without their guidance and insight on the usage of equipment, it would have been hard to carry out my experimentation.

Finally, I would like to thank all individuals involved directly or indirectly for the completion of this report.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Sorption, which is a general term introduced by J.W. McBain (Seader and Henley, 1999), includes selective transfer to the surface, and for into the bulk of liquid. Thus adsorption of gas into a non-porous membrane is also sorption operations. In a general sorption process, the sorbed solutes are referred to as sorbate & the sorbing agent is the sorbent. Adsorption process may be classified as purification or bulk separation, depending on the concentration in the feed fluid to the component adsorbed. Although there is no sharp dividing concentration, Keller suggested 10wt% (Seader and Henley, 1999). Early applications of adsorption involved only purification, for e.g.: adsorption with charred wood to improve the taste of water has been known for at least five centuries. Adsorption of gases by a solid charcoal was first described by C.W. Chele in 1773 (Seader and Henley, 1999). Commercial applications of bulk separation by gas adsorption began in early 1920s. But did not escalate until the 1960s, following the invention by Milton of synthetic molecular sieve zeolites, which provide high adsorptive selectivity. Later the pressure swing cycle of Skarstrom, which made possible the efficient of operation of a fixed bed cyclic gas adsorption process (Seader and Henley, 1999). The commercial scale bulk separation of liquid mixtures also began in 1960s, following the invention by Broughton & Greshold of the simulated moving bed for adsorptive separation.

In a typical wastewater treatment flow sheet used by several industrial units in India, various stages of treatment include primary treatment, followed by secondary treatment, and tertiary treatment. The concentration of total dissolved solids increases during neutralization of the wastewater with acid/ alkali during primary treatment, which adversely affects the activity of microorganisms during biological treatment. The present study aims at demonstrating that adsorption as the first stage of treatment shall increase efficiency of the subsequent biological treatment. Experiments were carried out on different wastewater samples from chemical plants on adsorbents as activated carbon,

bentonite, and lignite. The effectiveness of adsorbents in the removal of refractory organics by way of reducing chemical oxygen demand and colour is evaluated.

1.2 Problem Statement

The treatment of wastewater containing colored contaminants has been a technological challenge for many decades. Large amounts of wastewater with high concentrations of persistent and toxic color discharged from the textile, paper, carpet, and printing industries are aesthetically and environmentally damaging. Due to the toxicity of most dyes to plants and micro-organisms, colored wastewater cannot be discharged without adequate treatment. Cationic dyes were tested as more toxic than anionic dyes. Chromium-based dyes can release chromium ions, which are carcinogenic in nature. As dyes have complex structures and synthetic origins and are designed to resist breakdown with time and exposure to sunlight, water, soap, and oxidizing agents, they cannot easily be removed by conventional physical, chemical, or biological wastewater treatment processes, such as flocculation–coagulation, ozonation, or aerobic or anaerobic digestion.

1.3 Objective and Scope of Study

The main objectives of this research are:

- To investigate and measure adsorption rate and adsorption capacity in different temperature for wastewater treatment.
- To develop hydrotalcite-derived Mg/Al mixed oxide for adsorption dye from wastewater.
- To determine the equilibrium adsorption capacities for various initial concentrations, C_o of dye, initial doses of adsorbent and varying initial temperature.

The scope of work for this project is to investigate and measure acid dye (wastewater) concentration and loading to plot adsorbent concentration versus time graph in order to determine adsorption rate and adsorption capacity. Acid blue will be acting as the acid dye.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while desorption is the reverse process.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.

2.2 Anionic Clays

The term clay is generally applied to a natural material with plastic properties, particles of very fine size, customarily those defined as particles smaller than two micrometers and very fine mineral fragments or particles composed mostly of hydrous-layer silicates of aluminum, though occasionally containing magnesium and iron. Although, in a broader sense, clay minerals can include virtually any mineral of the above-cited particle size, the definition adapted here is restricted to represent hydrous-layer silicates and some related short-range ordered aluminosilicates, both of which occur either exclusively or frequently in very fine-size grades.

Hydrotalcite, known as an anionic clay as the interlayer anions, most commonly carbonate, can be exchanged with a wide range of inorganic and organic anions. It is a type of layered doubled hydroxide (LDH), occurs as a natural mineral and can be synthesised by reacting dilute aqueous solutions of magnesium and aluminium chlorides with sodium carbonate. The material consists of stacks of mixed hydroxide layers of Mg

and Al, $[Mg_{1-x}Al_x(OH)_2]^{x+}$, which are positively charged and require the presence of interlayer anions to maintain overall charge neutrality. The anion exchange capacity of the material is controlled by the Mg^{2+}/Al^{3+} ratio. This material has attracted considerable attention recently, owing to its anion exchange ability as well as its applications as selective sorbents and potential catalysts.

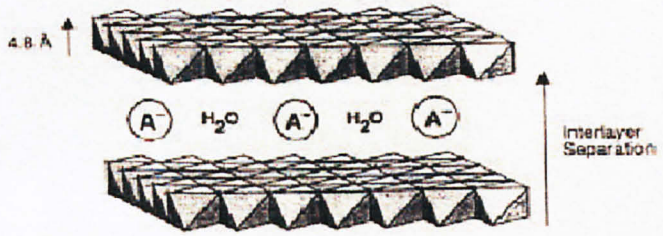


Figure 2.1 : Interlayer Structure of a Clay Hydrotalcite

2.3 Acid Dyes (Acid Blues)

Acid dye is a member of a class of dye that is applied from an acidic solution. In the home or art studio, the acid used in the dyebath is often vinegar (acetic acid) or citric acid. The uptake rate of the dye is controlled with the use of sodium chloride. Acid dyes are generally divided into three classes which depend on fastness requirements, level dyeing properties and economy. The classes overlap and generally depend on type of fiber to be coloured and also the process used. Acid dyes are thought to fix to fibers by hydrogen bonding, Van der Waals forces and ionic bonding. They are normally sold as the Sodium salt therefore they are in solution anionic. The strength (fastness) of this bond is related to the desire/ chemistry of the dye to remain dissolved in water over fixation to the fiber.

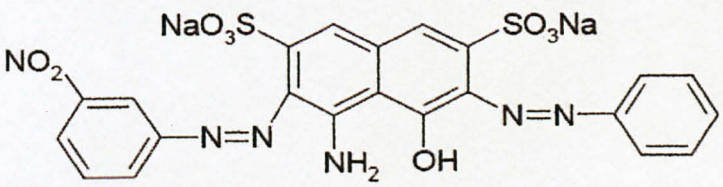


Figure 2.2 : Structure of Acid Blue 29

2.4 Characteristics of Dyes Used in Textile Industries

Although released in small fractions to the environment through wastewater, dyes are highly visible for even at very low concentrations and are undesirable. There are more than 100,000 commercially available dyes with over 7 x 10^5 tonnes on dyestuff produced annually. As if to add to the situation, the United States Department of Commerce has predicted a 3.5 fold increase in textile manufacturing between 1975 and 2020. A basic understanding of dyes and their composition will help in aiding their destruction. Dyes are defined as a substance that is used to impart color to materials of which it in advertently becomes an integral part. In order to impact color, an aromatic ring structure coupled with a side chain is usually required for resonance. It is these resonance structures that cause displacement or appearance of adsorption bands and are responsible for color. Correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome.

Chromogen is the aromatic structure containing benzene, naphthalene or anthracene rings. A chromophore group, on the other hand is a color giver and is represented by the following radicals, which form the basis for the chemical classification of dyes when coupled with the chromogen: azo (-N=N-); carbonyl (-C=O); carbon (-C=C-); carbon-nitrogen (C=NH or -CH=N-); nitroso (-NO- or N-OH); nitro (-NO_2 or NO-OH); and sulfur (C=S). But the chromogen-chromophore structure is most often not sufficient to impart solubility and cause adherence of dye to fiber. This is where the auxochrome plays an important role by bonding affinity groups and is also important in the use of classification of dyes. Examples for auxochrome include amine, hydroxyl, carboxyl, sulfonic radicals or their derivatives.

Basically most dyes almost always fall into three groups, namely cationic, nonionic and anionic type. Anionic types include direct, acid and reactive dyes. Among these, reactive and acid dyes are deemed the most problematic as they are brightly colored, water-soluble, tend to pass through conventional treatment systems unaffected and do not respond efficiently through conventional treatment systems. Nonionic dyes on

the other hand refer to disperse dyes, as they do not ionize in an aqueous medium. Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatics compounds.

2.5 Current Technologies for Treatment of Textile Effluent

Treatment of dyes in textile effluent can be achieved by both physical and chemical means. Unfortunately, decolorisation of textile effluent does not occur when treated aerobically by municipal sewerage system. Current methods utilized in dye removal can be seen in Table 2.1.

The main chemical method used to decolorize dyes in oxidative process with the main oxidizing agent being used is hydrogen peroxide (H_2O_2). The oxidizing agent first need to activate by some means and the method of decolorisation depends on the way of activation. Chemical oxidation removes dye by cleaving the aromatic ring of dye molecules.

Ozonation is a process which is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons. Photochemical method degrades dye molecules to carbon dioxide (CO_2) and water (H_2O) by UV treatment in the presence of hydrogen peroxide. Electrochemical destruction is a relatively new technique in which there is little or no consumption of chemicals and no sludge build up. It shows efficient and economical removal of dyes and a high efficiency for color removal and degradation of recalcitrant pollutants.

Physical treatment of dyes in textile effluent includes adsorption, reverse osmosis or coagulation/flocculation, to name a few. Of all these physical treatment, the adsorption technique has been used most widely to facilitate the treatment of wastewater. This technique is able to remove pollutants that cannot be achieved by conventional methods. Adsorption produces a high quality product and is a process which is economically feasible.

Table 2.1 Advantages and disadvantages of the current methods of dye removal from industrial effluents

Physical / Chemical Method	Advantages	Disadvantages
Fentos reagent	Effective decolorisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state; no alteration of volume	Short half life (20mins)
Photochemical	No sludge production	Formation of byproducts
NaOCl	Initiates and accelerates azo-bong cleavage	Release aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention time
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removal of all dye types	Concentrated sludge production
Ion exchange	Regeneration; no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved oxygen
Electrokinetic coagulation	Economically feasible	High sludge production

2.6 Adsorption for Removal of Dyes from Effluent

The application of the adsorption process in liquid stream is used to treat industrial wastewater containing organic, dye and heavy metal ions and remove taste and odor from water. Its application in gaseous stream is often to remove odors.

The main advantages of adsorption over other conventional methods includes requirement for less land area (approximately half to quarter of what is required in a biological system), lower sensitivity to diurnal variation, not getting affected by toxic chemicals, greater flexibility in the design and operation and superior removal of organic contaminants.

2.7 Theory of Adsorption

Adsorption is defined as a process by which material accumulates at the interface between two phases and these two phases can be liquid-liquid, liquid-solid, gas-liquid and gas-solid. The adsorbing phase is known as adsorbent whereas the substance being adsorbed is termed as adsorbate.

Adsorption occurs at the surface since it reduces the imbalance of attractive forces and therefore, the surface free energy of the heterogeneous system. Two important properties in adsorption system include the adsorptive capacity of a given amount of adsorbent for a particular solute and the adsorption rate at which that solute is taken of the solution. Adsorption rate depends on several factors among which are the size and porous structure of the adsorbents, size and structure of the solute molecule, concentration of solute in solution and temperature of the solution. Adsorptive capacity on the other hand influenced by factors such as pH, dye-adsorbent interaction, particle size of adsorbent, adsorbent surface area, contact time and temperature.

The adsorption process on an adsorbent usually proceeds in three consecutive steps. Firstly is the transport of solute from the bulk of the solution to the outer surface of the film surrounding the particle-bulk transport. Next is the transport of solute within the film-film transport. Finally is the transport in the interior of the particle-intra-particle transport.

Thus if C_0 is the initial concentration, C_e is the concentration of solute after equilibrium and *m* is the mass of adsorbent present, then the amount of solute adsorbed per unit weight of adsorbent is given as :

$$q_e = \frac{(C_o - C_e)\, xV}{m} \qquad (2.1)$$

where *V* is the volume of the solution used in batch.

The relationship between the quantity of adsorbate per unit of adsorbent, q_e and the equilibrium concentration in solution, C_e is called an adsorption isotherm. The equilibrium-adsorbed amount of the adsorbent is a function of both the characteristics and concentration of the adsorbate depending on the temperature.

Equations that are normally used to describe the experimental adsorption rate are normally those developed by Freundlich and Langmuir. Freundlich isotherm is an empirical expression and has no physical basis; hence the equilibrium relationship proposed by Freundlich is only valid when the adsorption is a purely physical process without any changes in the configuration of the molecules in the adsorbed state. The equilibrium equation of this model is as follows :

$$q_e = K_F * C_e^{\,1/n} \qquad (2.2)$$

where q_e represents the equilibrium adsorbed amount on the adsorbent, C_e the equilibrium concentration and K_F and n are the empirical constant depending on the nature of adsorbate and adsorbent. The constant K_F is an approximate indicator of adsorption capacity while 1/n is a function of the strength of adsorption, i.e mechanism of adsorption. The constant in the model can be obtained by linearising equation 2.2

$$\ln q_e = K_F + 1/n \ln C_e \qquad (2.3)$$

The common form for the Langmuir isotherm is

$$q_e = \frac{q_0 b C_e}{1 + bC_0} \qquad (2.4)$$

Where q_0 represent the saturation limit and b is a temperature dependent equilibrium constant. The constant q_0 corresponds on the surface concentration at monolayer coverage and represents the maximum value of q_0 that can be achieved as C_e is increased. The constant *b* is related to energy of adsorption and increases as the strength of the adsorption band increases. In order to evaluate the Langmuir constant, a linearised form of equation 2.4 is used

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \qquad (2.5)$$

A plot of $1/q_e$ vs $1/C_e$ will yield a straight line for data which fits the Langmuir expression. Hence the Langmuir constants can be calculated from the gradient and the intercept.

2.8 Classifications of Adsorbents

By far the most effective adsorbent utilized would be activated carbon. It is very effective for adsorbing cationic, mordant and acid dyes to slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes. Activated carbon is an exceptionally versatile adsorbent because of its large surface area, favorable pore size, universal adsorption effect and high degree of surface reactivity. Unfortunately its high cost acts as a damper to its application. Spent activated carbon has to be reactivated prior to disposal; otherwise special considerations have to be made. Also reactivated activated carbon normally losses about 10% - 15% of the sorbent. This is led researches of this area to focus on alternative adsorbents which are just as efficient as activated carbon but more economical.

Peat has proven to be a good alternative adsorbent. It has the ability to adsorb transition metals and polar organic compounds. It requires no activation and costs much lesser than activated carbon. Spent peat may be burned and utilized for steam rising. Wood chips show how a good adsorption capacity for acid dyes although due to their hardness, it is not good as other available sorbents. Consequently numerous low cost alternatives have been studied including the equilibrium sorption of dyes on chitin and chitosan, banana pith, bagasse pith, barley husk, soil and china clay.

2.9 Role of Clays as Adsorbents

In this study the effectiveness of a clay-like material in removing dye from a synthetic effluent has been investigated. Clay is a general term for highly variable group of natural materials that are soft, earthy, extremely fine-grained and usually plastic when moist. Alkalies such as sodium, lithium and potassium and alkaline earths such as magnesium, calcium and barium are often present in the molecular structure of clays and have a significant effect in the physical and chemical properties.

Clays occurring in the nature rarely comprise pure, single clay minerals. They usually contain a variety of non-clay impurities such as quartz, calcite, mica, and feldspar. Most clay minerals involve two basic types of structure in their units in their atomic structures. The manner in which these units are combined and the type of exchangeable atoms is present will play a significant role in the type of clay mineral that forms. The major clay resources include kaolinite, bentonite , halloysite and illite.

The characteristics common to all clay minerals derive from their physical, chemical and structural composition. Clay minerals have a great affinity for water. Some swell easily and may be even double in thickness when wet. Most have ability to soak up ions from a solution and release the ions later when conditions change.

Another important property of clay, the ability to exchange ions, relates to the charged surface of clay minerals. Ions can be attracted to the surface of clay particle or

taken up within the structure of these minerals. The property of clay minerals that causes ions in solution to be fixed on clay surfaces or within internal site applies to all types of ions including organic molecules. Clays can be an important vehicle for transporting and widely dispersing contaminants from one area to another. For this reason and also considering the fact that clay is widely available, it was used in this study to test its effectiveness in removing dyes from wastewater effluents.

2.10 Hydrotalcite-like Materials (Layered-Double Hydroxide)

Hydrotalcite (HT) has attracted much attention during development of new environmentally friendly adsorbents. Hydrotalcites are examples of so called layered double hydroxides (LDH) or anionic clays, consisting of brucite like structures. Anionic clays are the most promising adsorbent for many adsorption process of industrial interest, complementary of those cationic clays.

There are many names used based on the composition and polytype form of the minerals. The general terms, hydrotalcite type (HT) compounds or layered double hydroxides (LDH's) are widely used. The term 'hydrotalcite-type (HT) compounds' is used because extensive characterizations have carried out on hydrotalcite, a MG/Al hydroxycarbonate rather than on similar compounds. On top of that, the Mg/Al HT is easily and inexpensive to synthesize.

Table 2.2 Composition, crystallographic parameters and symmetry for some natural anionic clays

Mineral	Chemical Composition	Unit Cell Parameters		Symmetry
		a (nm)	c (nm)	
Hydrotalcite	$Mg_6 Al_2 (OH)_{16} CO_3 . 4H_2O$	0.3054	2.281	3R
Manasseite	$Mg_6 Al_2 (OH)_{16} CO_3 . 4H_2O$	0.3100	1.560	2H
Pyroaurite	$Mg_6 Fe_2 (OH)_{16} CO_3 . 4H_2O$	0.3109	2.341	3R
Sjogrenite	$Mg_6 Fe_2 (OH)_{16} CO_3 . 4H_2O$	0.3113	1.561	2H
Stichtite	$Mg_6 Cr_2 (OH)_{16} CO_3 . 4H_2O$	0.3100	2.340	3R

Barbertonite	$Mg_6 Cr_2 (OH)_{16} CO_3 . 4H_2O$	0.3100	1.560	2H
Takovite	$Ni_6 Al_2 (OH)_{16} CO_3 . 4H_2O$	0.3025	2.259	3R
Reevite	$Ni_6 Fe_2 (OH)_{16} CO_3 . 4H_2O$	0.3081	2.305	3R
Meixnerite	$Mg_6 Al_2 (OH)_{16} (OH)_2 . 4H_2O$	0.3046	2.292	3R
Coaglinite	$Mg_6 Fe_2 (OH)_{24} CO_3 . 2H_2O$	0.3120	3.750	3R

Hydrotalcite crystallize with a rhombohedral 3R stacking sequence, the parametes of the unit cell being *a* and $c = 3c'$, where c' is the thickness of one layer consisting of a brucite-like sheet and one interlayer, anions are located between two layers, originally equipped by water molecule.

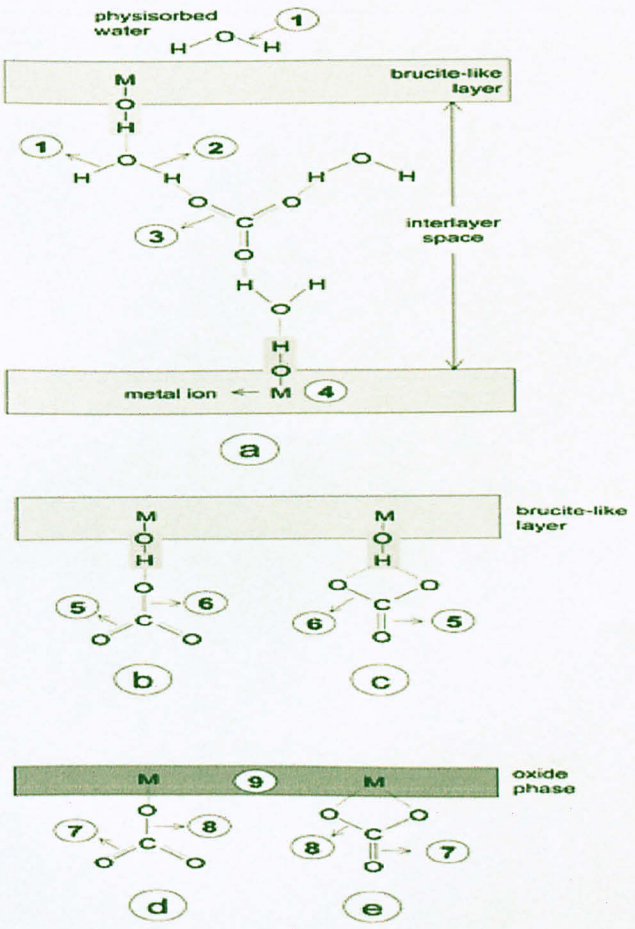


Figure 2.3 : Diagram of a Clay Hydrotalcite

Hydrotalcite like material are represented by the general formula :

$$[\,M_{1-x}^{2+}\,M_x^{3+}\,(OH)_2\,]^{x+}\,A_{x/n}^{n-}\,yH_2O$$

where M^{2+} is divalent cation

M^{3+} is trivalent action

A^{n-} is the interlayer cation

X is molar ratio of $\dfrac{M^{3+}}{M^{2+} + M^{3+}}$

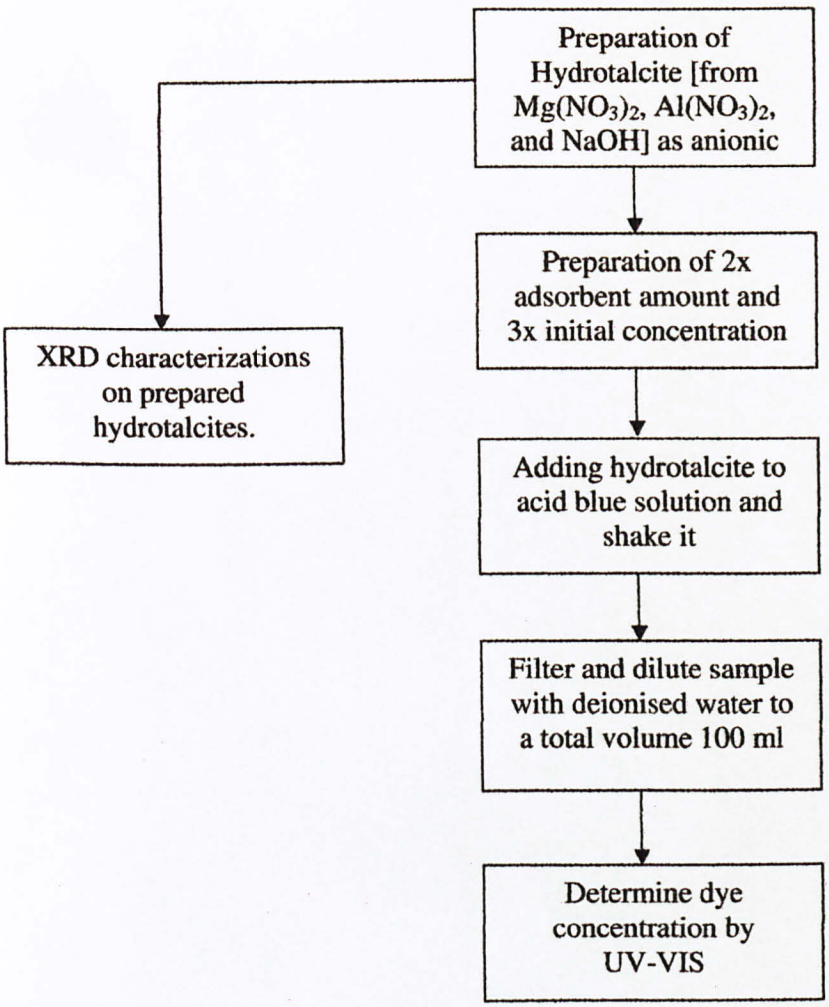
Classical co-precipitation method at constant pH can be used to prepare LDH's from nitrate salts. The co-preciptation method is different from sequential precipitation. Using the co-precipitation method, a well-defined compound is possible. This compound may serve as a chemical precursor from which a final solid is obtained. Is sequential precipitation, separate chemical compounds (M^{2+} and M^{3+} species precipitates) are formed.

Synthetic anionic clays, in its original form or after thermal decomposition are used in many industrial applications. It is projected that in future, its use will span over a wide range of applications, probably even in total unexpected areas. Finally LDH's can also act as sorbents and ion exchangers.

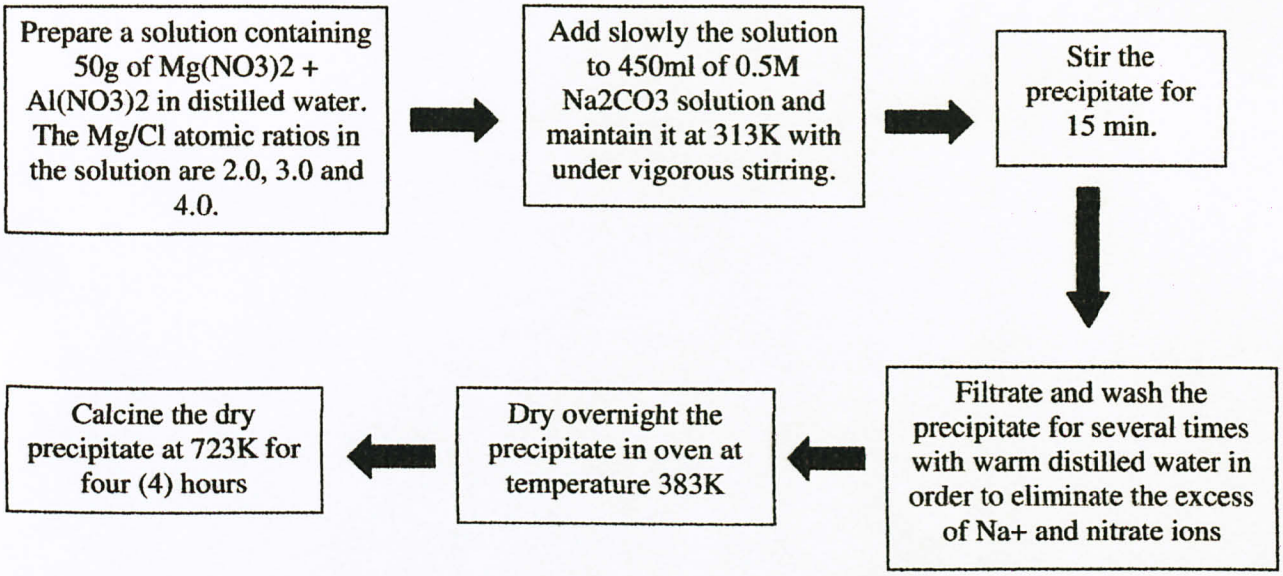
CHAPTER 3

METHODOLOGY

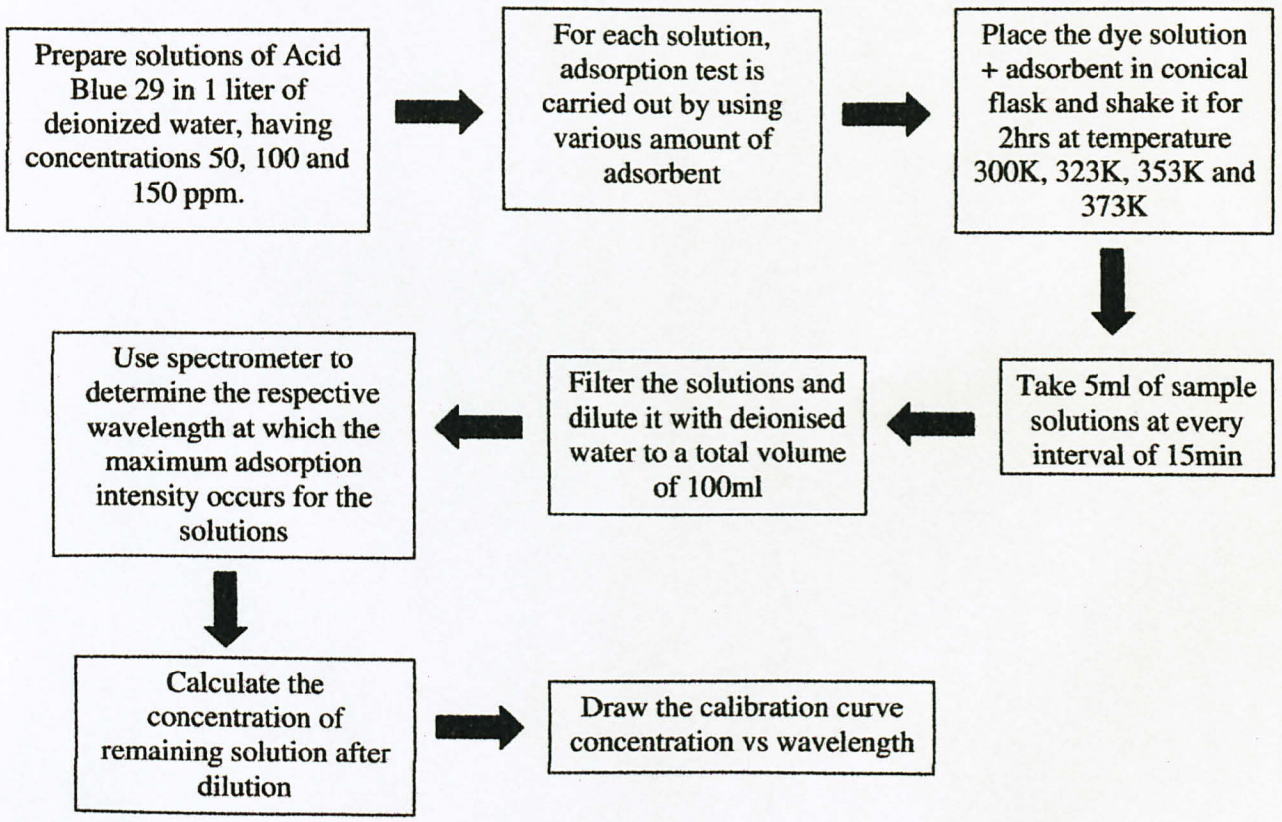
3.1 MATERIALS AND EXPERIMENTALS METHOD



3.1.1 Preparing adsorbent – Hydrotalcite as anionic clay using Mg(NO3)2, Al(NO3)2 and Na2CO3



3.1.2 Adsorption test



CHAPTER 4
RESULTS AND DISCUSSION

4.1 Work Completed

As of this time, I have completed the following research work and amputating the sections of the final report together. Here is a breakdown of the work that I have done so far.

4.1.1 Calculation for Material Balance

For amount of $Mg(NO_3)_2 . 6H_2O$ and $Al(NO_3)_3 . 9H_2O$

$2Mg(NO_3)_2 . 6H_2O + Na_2(CO_3)_2.10H_2O \rightarrow Mg_2(OH)_2CO_3 + NaNO_3 + H_2O + HCO_3$

$Al(NO_3)_3 . 9H_2O + Na_2(CO_3)_2 . 10H_2O \rightarrow Al(OH)CO_3 + NaNO_3 + H_2O + HCO_3$

Materials	Symbol	MW (g/mol)
$Mg(NO_3)_2 . 6H_2O$	M	256.330
$Al(NO_3)_3 . 9H_2O$	A	375.010
$Na_2(CO_3)_2.10H_2O$	N	285.990

Mol Ratio (M/A) = 0.5, 1.0, 2.0, 3.0

Total Amount (M + A) = 50g

M = x , A = y

x + y = 50 (Eq. 1)

$$\text{Mol Ratio, MR} = \frac{x/256.330}{y/375.010} \rightarrow x = MR*256.330y / 375.010$$

MR = 0.5

$x = 0.342y$ (Eq. 2)

Substitute eq.2 into eq.1

$x + y = 50$

$0.342y + y = 50$

$1.342y = 50$

$y_1 = 37.264g$; $x_1 = 12.763g$

MR = 1.0

$x = 0.684y$ (Eq. 3)

Substitute eq.3 into eq.1

$x + y = 50$

$0.684y + y = 50$

$1.684y = 50$

$y_2 = 29.700g$; $x_2 = 20.300g$

MR = 2.0

$x = 1.36y$ (Eq. 4)

Substitute eq.4 into eq.1

$x + y = 50$

$1.36y + y = 50$

$2.36y = 50$

$y_4 = 21.123g$; $x_4 = 28.877g$

MR = 3.0

$x = 2.051y$ (Eq. 5)

Substitute eq.5 into eq.1

$x + y = 50$

$2.051y + y = 50$

$3.051y = 50$

$y_5 = 16.390g$; $x_5 = 33.610g$

Mol Ratio	Mass M (g)	Mass A (g)
0.5	12.736	37.264
1.0	20.300	29.700
2.0	28.877	21.123
3.0	33.610	16.390

For amount of $Na_2(CO_3)_2.10H_2O$ (N) required

Mol Ratio

Mg : Na = 2 : 1 M = x; A = y; N = z

Al : Na = 1 : 1

Mg = 2

Na 1

$\frac{x / 256.330}{z / 285.990} = 2 \rightarrow x = 2(z / 285.99)(256.33)$

$x = 1.793z$

$z_1 = x / 1.793 \rightarrow z_1 = 0.558x$

Al = 1

Na

$\frac{x / 375.010}{z / 285.990} = 1 \rightarrow y = (z / 285.990)(256.33)$

$y = 1.311z$

$z_2 = y / 1.311 \rightarrow z_2 = 0.763y$

Total z is

$z = z_1 + z_2$

$z = 0.558x + 0.763y \rightarrow$ must add 10% more then need to multiply 1.1 (Eq. 6)

For amount H_2O to make $Na_2(CO_3)_2.10H_2O$ (0.5M)

z = mass N

x = mass M $\qquad z = (0.558x + 0.763y)(1.1)$ (Eq. 6)

y = mass A

mol N = mass N / MW N $\qquad M = 0.5M \rightarrow M = \frac{\text{mol}}{\text{L}}$

For x = 12.736g ; y = 37.264g

Substitute in eq.6

$m_{N1} = 39.093g$; $mol_{N1} = 0.137mol$

Volume DW_{N1} = 0.137mol / 0.5M

= 0.274L

= 274mL

For x = 20.300g ; y = 29.700g

Substitute in eq.6

$m_{N2} = 37.388g$; $m_{N2} = 0.131mol$

Volume DW_{N2} = 0.131mol / 0.5M

= 0.262L

= 262mL

For x = 28.877g ; y = 21.123g

Substitute in eq.6

$m_{N3} = 25.453g$; $mol_{N3} = 0.124mol$

Volume DW_{N1} = 0.124mol / 0.5M

= 0.248L

= 248mL

For x = 33.610g ; y = 16.390g

Substitute in eq.6

$m_{N4} = 34.386g$; $m_{N4} = 0.120$ mol

Volume DW_{N2} = 0.120mol / 0.5M

= 0.240L

= 240mL

4.1.2 Dye calibration curve and analysis

The dye solutions with various concentrations had been calculated as

$$\text{Concentration (ppm)} = \frac{\text{Amount of solute}}{\text{Amount of solvent}} \times 10^6$$

$$\text{Amount of solute (dye)} = \frac{\text{Concentration (ppm)} \times \text{Amount of solvent}}{10^6}$$

$$= \frac{(20) \times (50\text{ml})}{10^6}$$

$$= 1 \times 10^{-3} = 0.001$$

Amount of solvent that has been used in this calculation is 50ml deionized water.

Concentration (ppm)	Mass Acid Blue 29 (g)	Absorbance
0	0	0
20	0.001	1.47
40	0.002	4.89
60	0.003	8.75
80	0.004	10.92
100	0.005	13.61
120	0.006	16.47
140	0.007	19.56
160	0.008	23.84
200	0.010	29.24

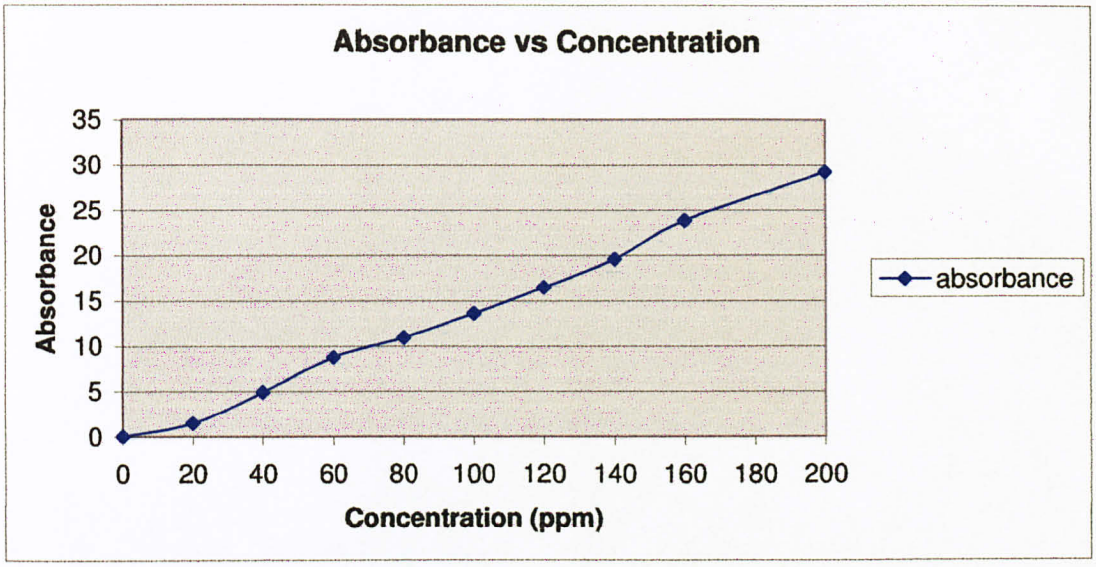


Figure 4.1: Absorbance vs Concentration (ppm)

4.1.3 Adsorption Test

Adsorption (%) = $[(A_0 - A)/A_0] \times 100$

which A_0 = initial absorbance at 602nm wavelength

A = final absorbance

Effect of Initial Concentration

The effect of the initial concentration of dye on the extent of the removal of Acid Blue 29 dye on hydrotalcite was studied. The process for Acid Blue 29 to be removed will be found to be very rapidly initially and remain constant after concentration reached equilibrium. Since the absorbance value decreasing and inversely proportional with the time, hence the amount of dye removed will be increasing with the increase in initial concentration. This observation may be due to availability of active sites for high initial concentration of dyes, which leads to the increasing in immediate solute adsorption.

The results of absorbance below are determined by UV-VIS Spectrophotometer by using 602nm as Acid Blue 29 wavelength.

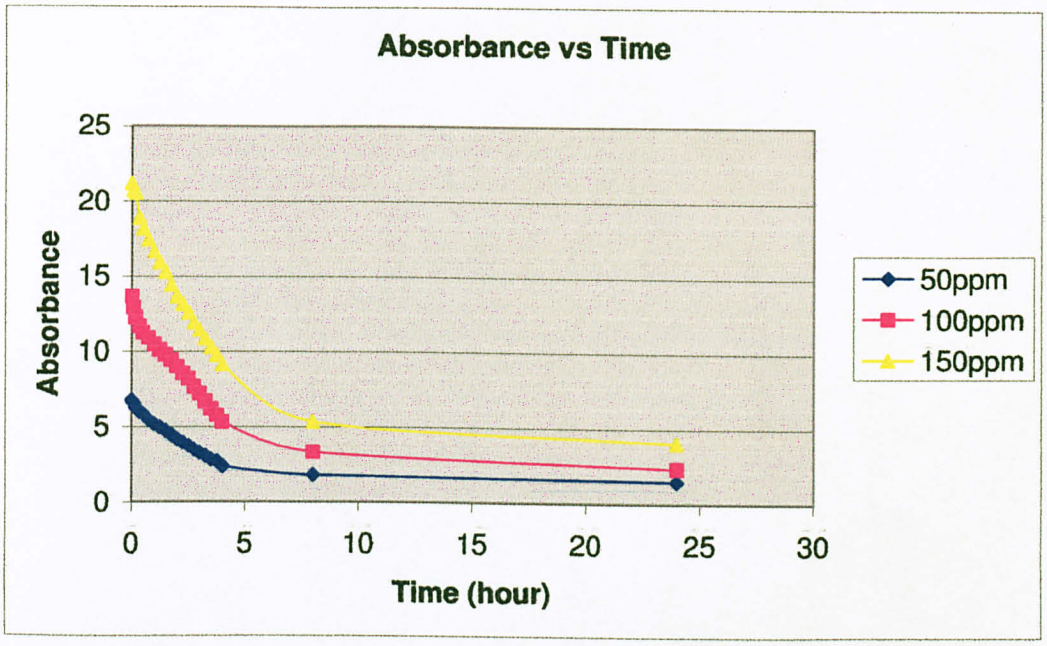


Figure 4.2: Absorbance vs Time (30°C, 0.2g/60ml of M/A 2.0)

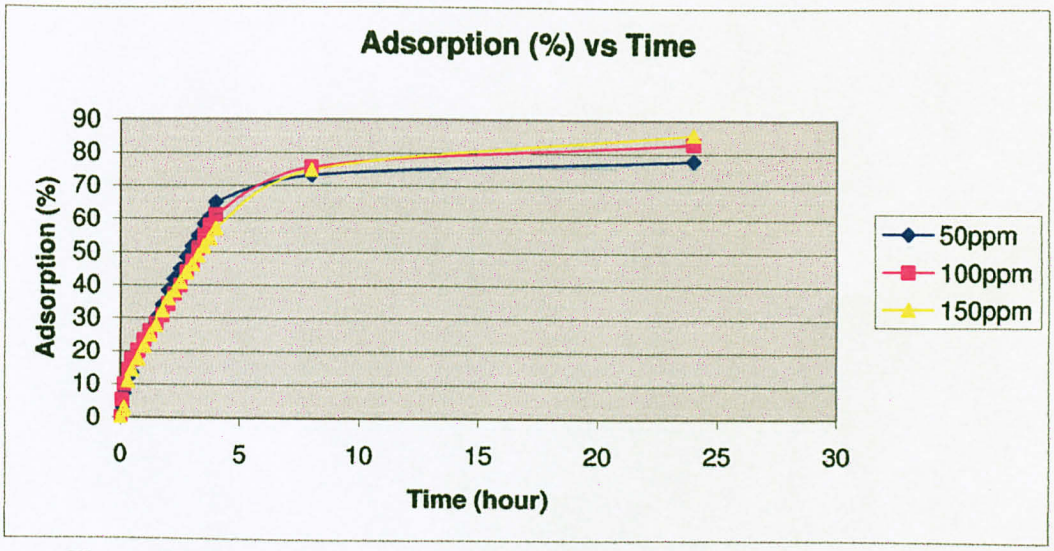


Figure 4.3: Percentage of Adsorption vs Time (30°C, 0.2g/60ml of M/A 2.0)

Effect of Contact Time

The adsorption of Acid Blue 29 dyes at different initial concentrations of hydrotalcite adsorbent were studied to assess the contact time necessary for the adsorption systems to reach equilibrium. The time need for equilibrium adsorption should be less than five hours for the dye. For experimental purposes, all the different experimental systems will be given a contact time in excess of this period, 24 hours.

The rate of removal of adsorbate from a solution is controlled mainly by the rate of transport of the adsorbate species from the exterior sites to the interior sites of the adsorbent particles. A monolayer of adsorbate normally formed on the surface of the adsorbent. Therefore after a certain period of time, the adsorbent becomes saturated and removal of dye becomes constant.

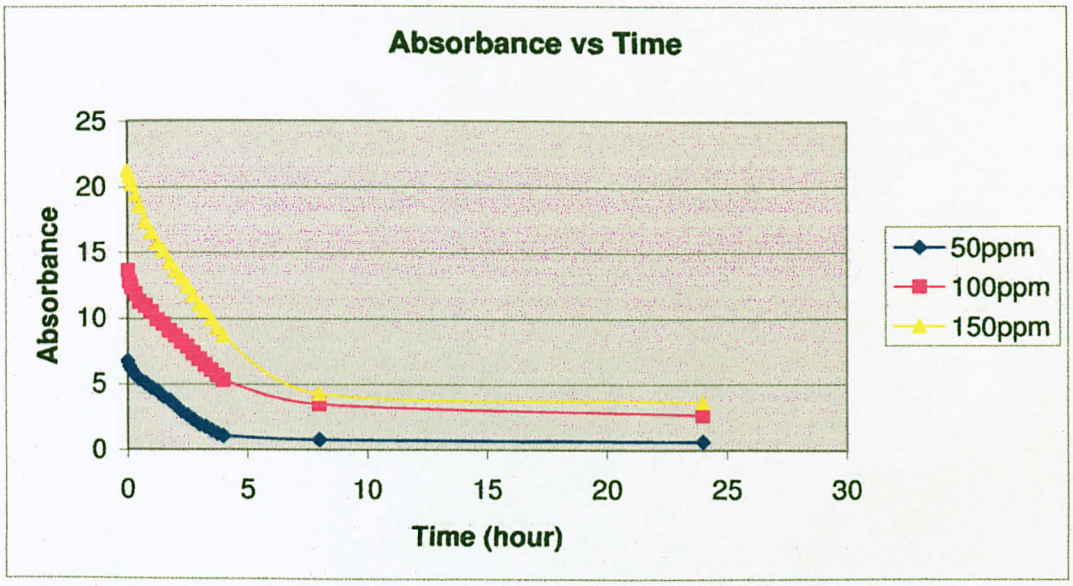


Figure 4.4: Absorbance vs Time (30°C, 0.2g/60ml of M/A 3.0)

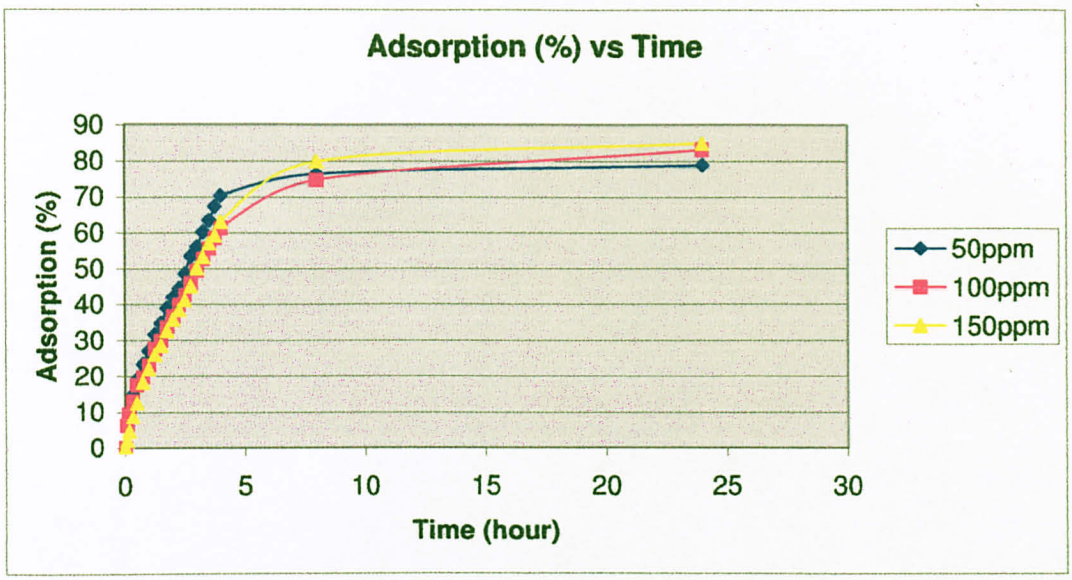


Figure 4.5: Percentage of Adsorption vs Time (30°C, 0.2g/60ml of M/A 3.0)

Effect of Adsorbent Dose

Since the adsorbent dose increase, the percentage of adsorption for Acid Blue 29 hydrotalcite system will be increase. This increment in adsorption may be due to the increase in surface area and the availability of more adsorption sites. The equilibrium value of the amount adsorbed also will be increase with increasing in dose.

From the researches, it shows that the effect of adsorbent dose significantly affects the rate of adsorption of the Acid Blue 29 hydrotalcite system. Also indicates that removal of the Acid Blue 29 hydrotalcite system is more favourable based on the percent of dye removed.

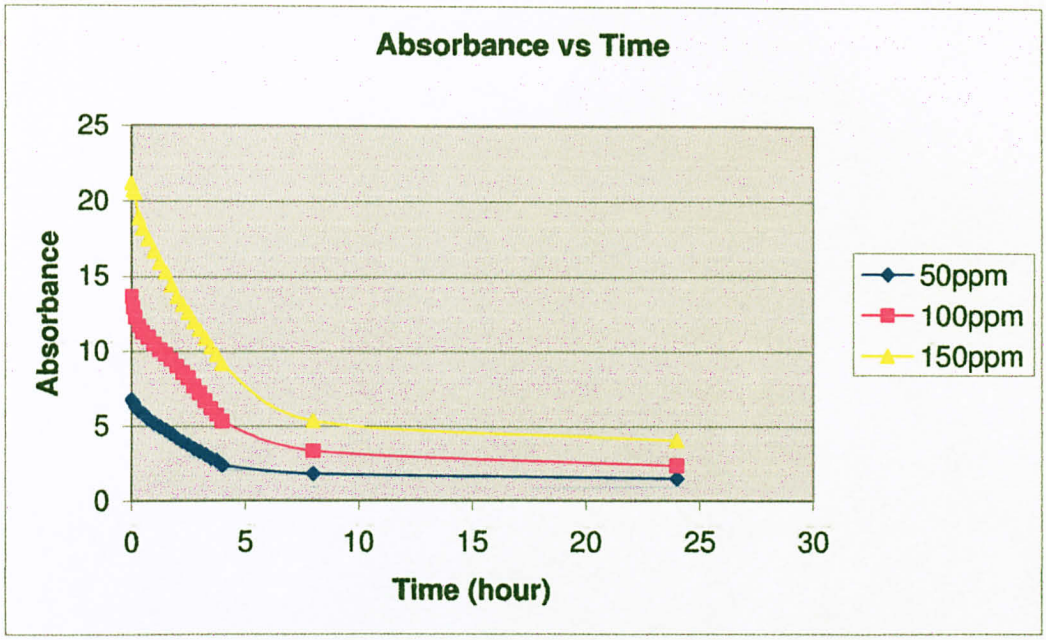


Figure 4.6: Absorbance vs Time (30°C, 0.2g/60ml of M/A 2.0)

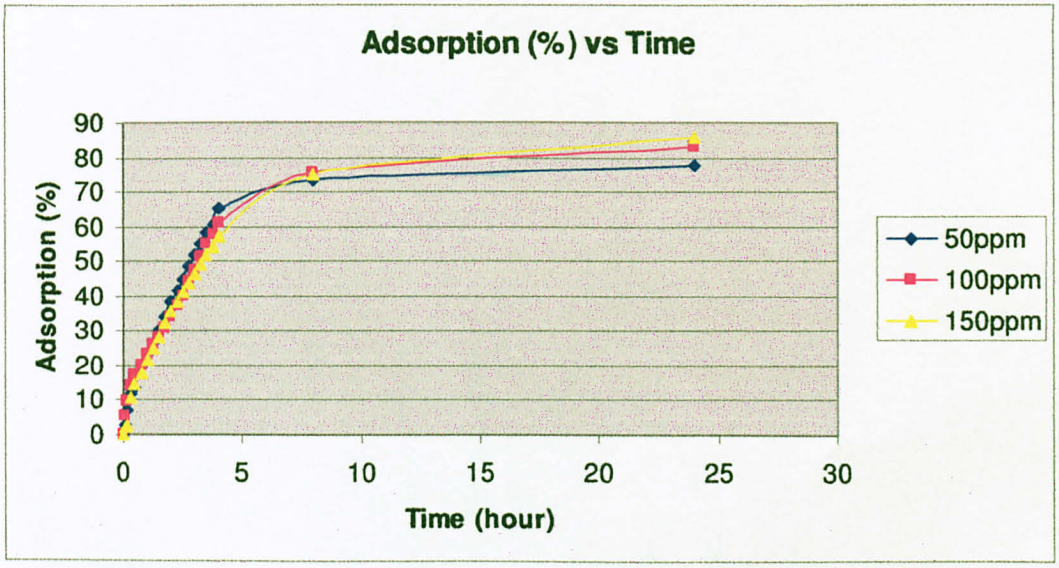


Figure 4.7: Percentage of Adsorption vs Time (30°C, 0.2g/60ml of M/A 2.0)

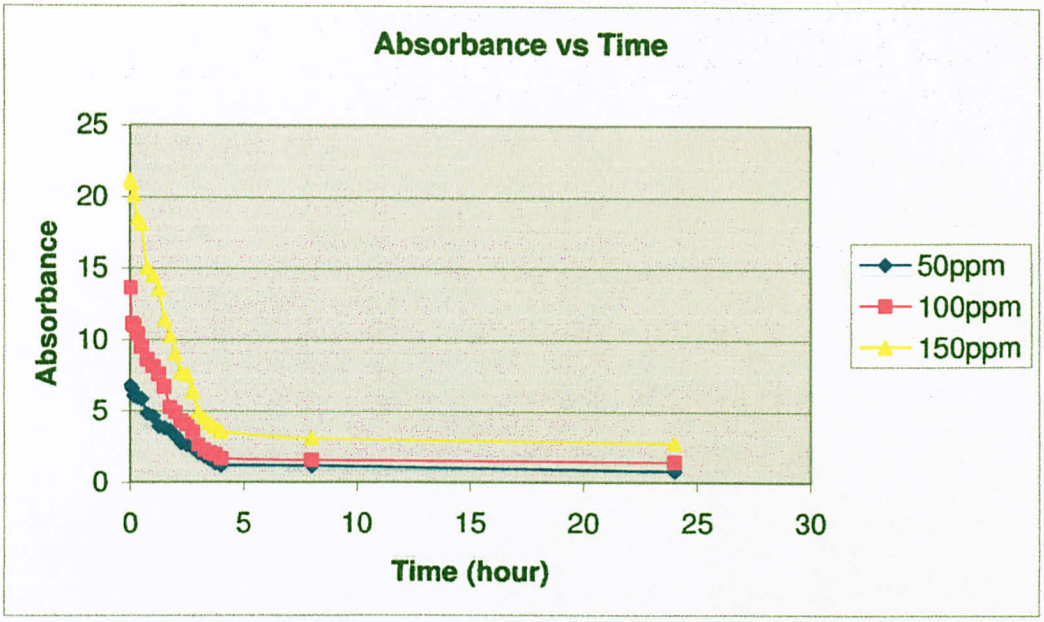


Figure 4.8: Absorbance vs Time (30°C, 0.4g/60ml of M/A 2.0)

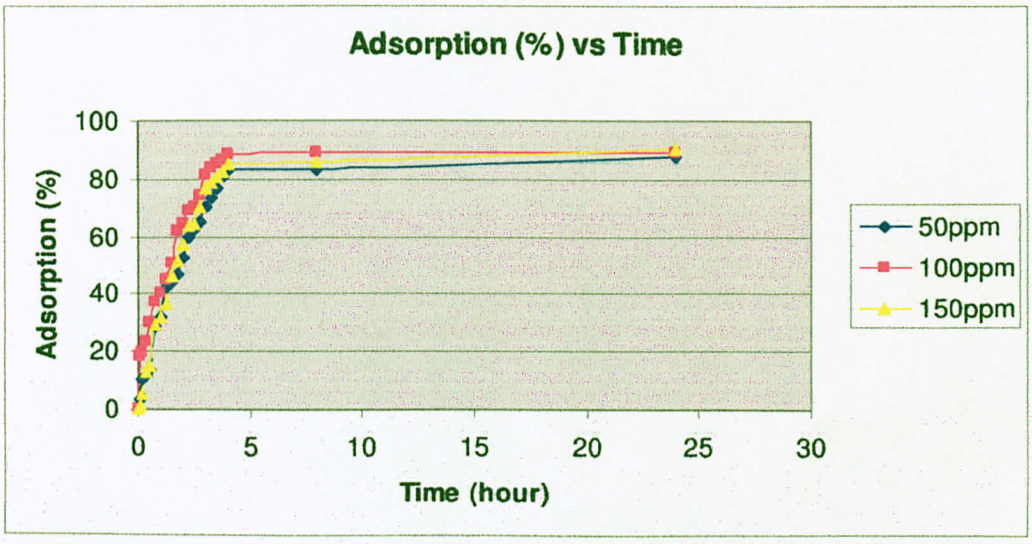


Figure 4.9: Percentage of Adsorption vs Time (30°C, 0.4g/60ml of M/A 2.0)

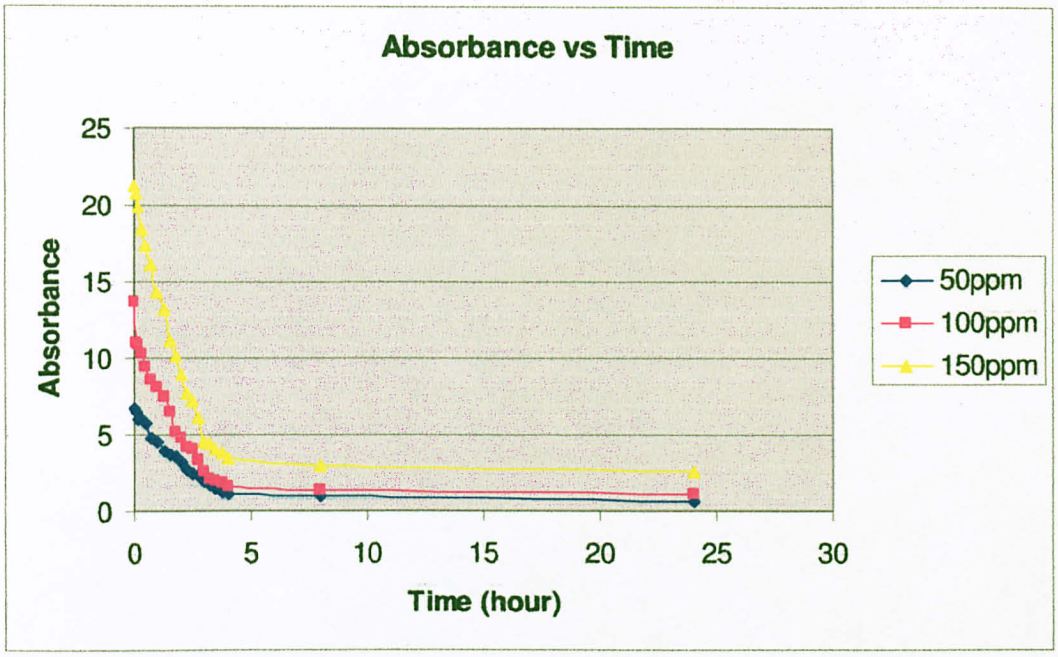


Figure 4.10: Absorbance vs Time (30°C, 0.6g/60ml of M/A 2.0)

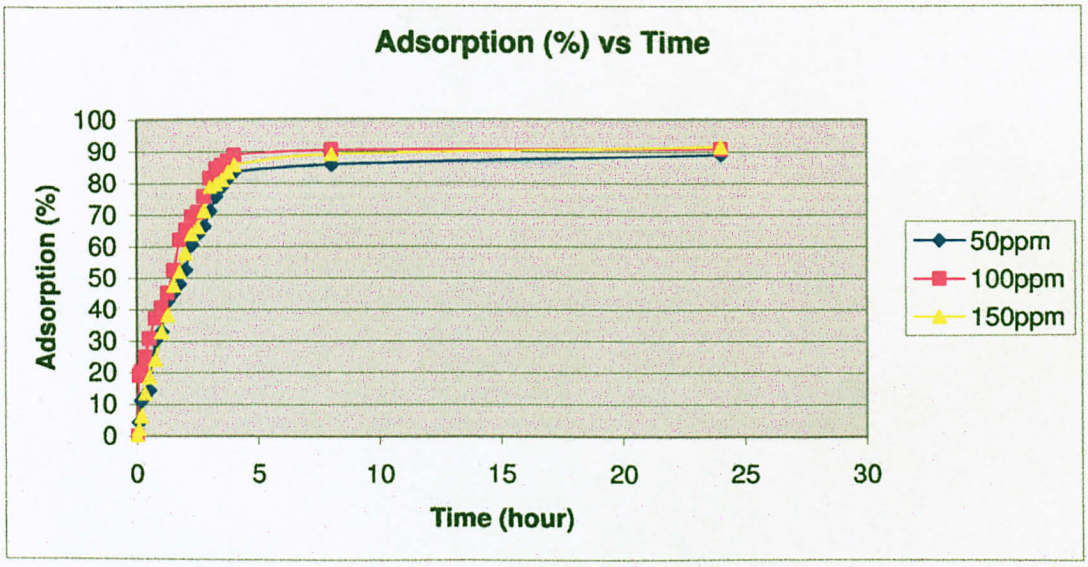


Figure 4.11: Percentage of Adsorption vs Time (30°C, 0.6g/60ml of M/A 2.0)

Effect of Temperature

The uptake of Acid Blue 29 hydrotalcite system will be varying as the temperature of the system increasing. This observation of increase in adsorption could be due to a few factors. When temperature is increase, the kinetic energy will be increasing also the enhanced rate of intra-particle diffusion of sorbate. It will make the changes in pore size.

There will be a slightly decreasing in dye uptake that could actually mean that the dye-hydrotalcite system might be exothermic. The adsorption rate will be decreasing if there are more increasing temperature after the effective temperature for the dye-hydrotalcite system.

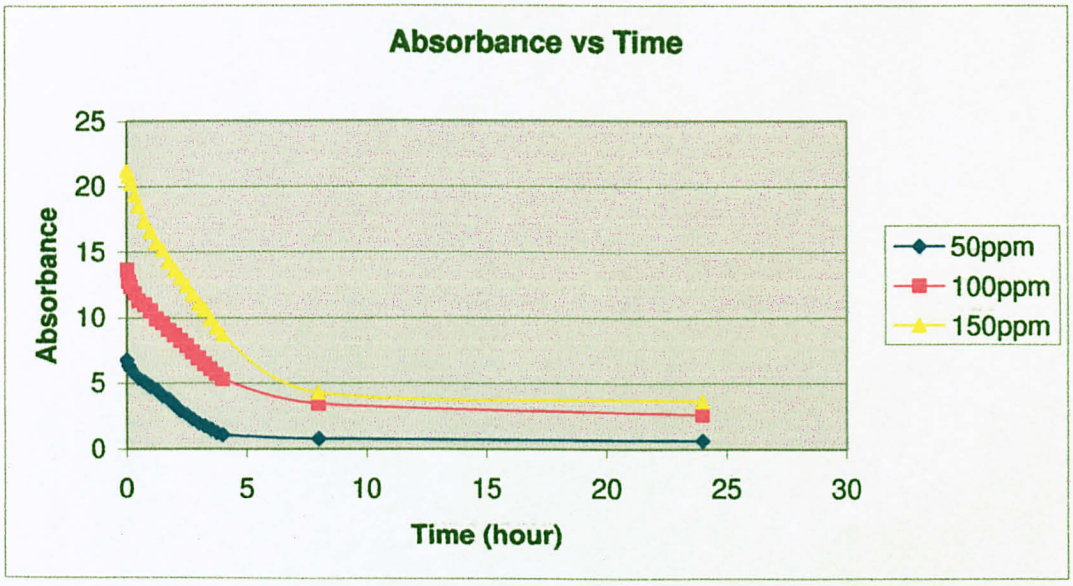


Figure 4.12: Absorbance vs Time (30°C, 0.2g/60ml of M/A 3.0)

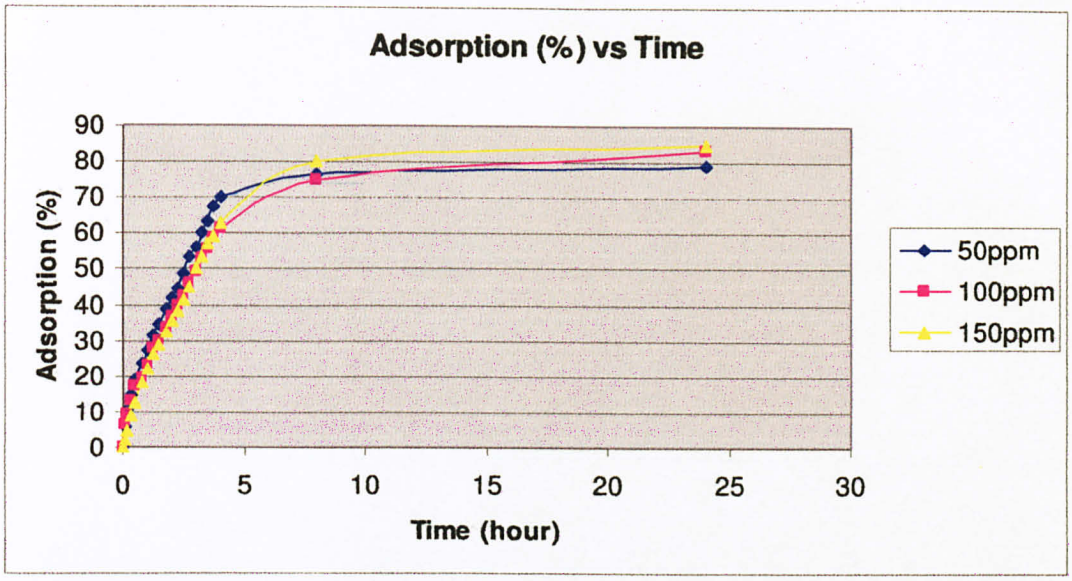


Figure 4.13: Percentage of Adsorption vs Time (30°C, 0.2g/60ml of M/A 3.0)

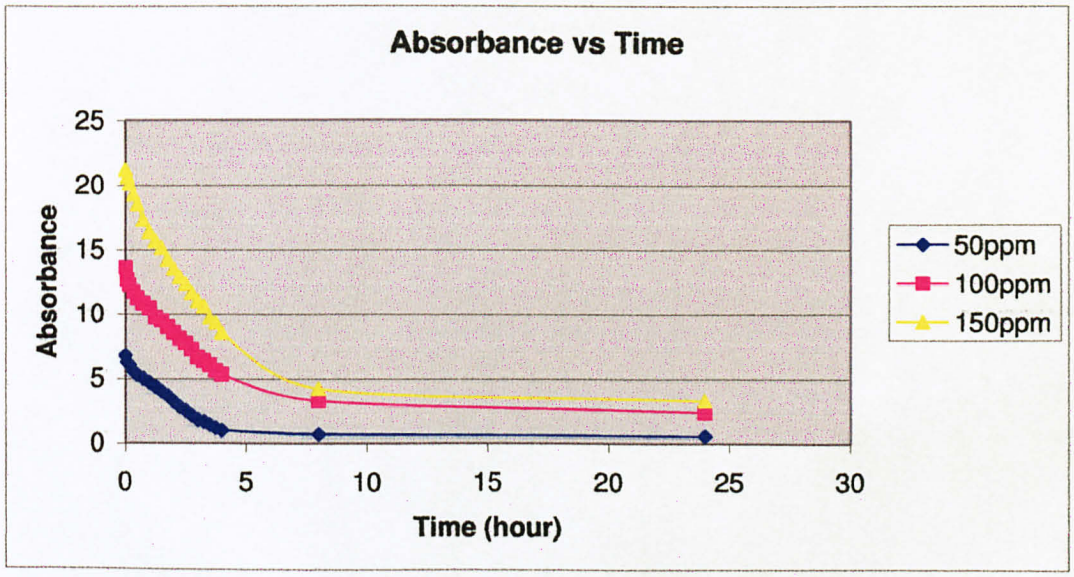


Figure 4.14: Absorbance vs Time (50°C, 0.2g/60ml of M/A 3.0)

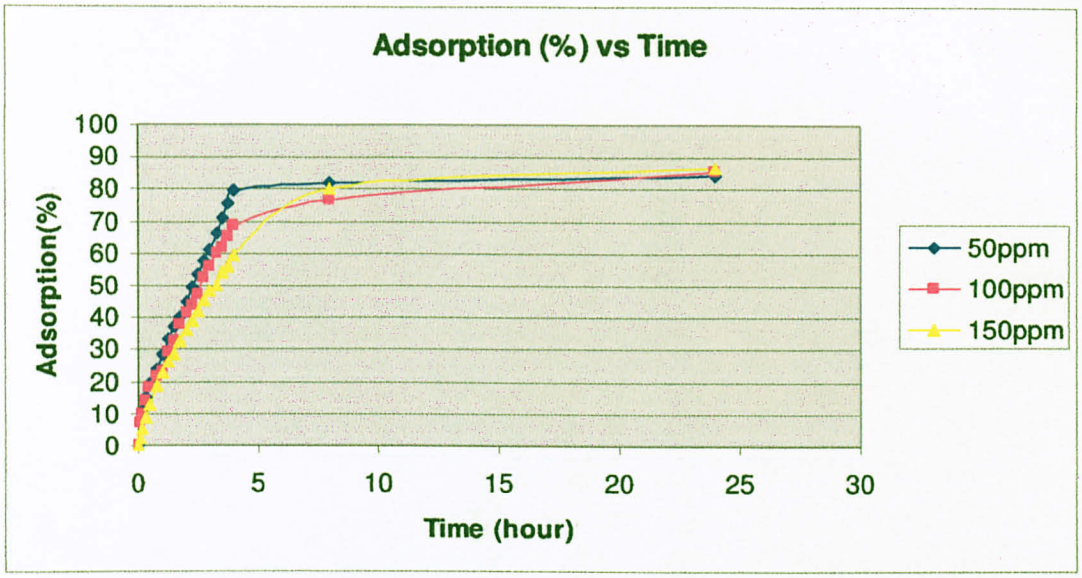


Figure 4.15: Percentage of Adsorption vs Time (50°C, 0.2g/60ml of M/A 3.0)

Adsorption Capacity

The graph shows that adsorption change when the parameters also change. Adsorption increases when adsorbent amount and initial concentration increase.

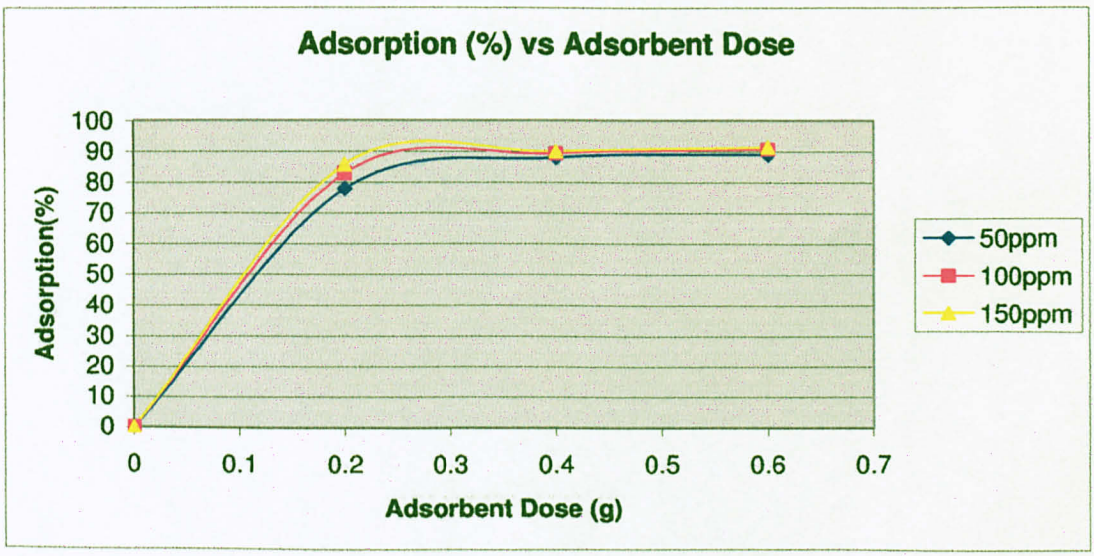


Figure 4.16: Percentage of Adsorption vs Adsorbent Dose

CHAPTER 5
CONCLUSION

Adsorption studies on Acid Blue 29 dye have shown that hydrotalcite is a potential substitute for activated carbon for dye removal from an aqueous solution. As the temperature of the dye-hydrotalcite system is increased, the amount of dye removed increases but only at certain temperature and then it proceeds to decrease as temperature is increased. It is important to find the optimum operating condition of a system to ensure maximum removal of dye. Removal of dye increased with the increase in amount of hydrotalcite used.

The mechanism of adsorption for the dye can be assumed to involve the three following steps:

i. Migration of the dye from the bulk of the solution to the surface of the adsorbent
ii. Adsorption of dye at an active site on the surface of hydrotalcite
iii. Intra-particle diffusion of dye into the interior pores of the hydrotalcite

Therefore hydrotalcite can be used as a low-cost adsorbent as an alternative to activated carbon for the removal of dye from wastewater, in general and for the removal of Acid Blue 29 in particular. Hydrotalcite can be used as a method to remove the treatment system. This way is quite economical because hydrotalcite which is cheap, can remove the bulk of dye from solution first so that lesser activated carbon can be used to remove the remaining dyes from the solution.

CHAPTER 6
RECOMMENDATION

Hydrotalcite on its own, without any modifications has proven to be good substitute for activated carbon. This study only focused on the use of hydrotalcite in its original form. Thus it is recommended that the hydrotalcite be modified using different available methods and to test its efficiency further. For example, soaking it in an acidic solution overnight and then drying it can modify the hydrotalcite. Modifications is not only limited to this method as there are extensive modification methods available in literature. Also since the main aim of any project is to test its applicability in a real life situation, it is good to test the hydrotalcite directly on actual wastewater from industry itself.

Thus the experiments can be repeated with other dyes such as basic and reactive dyes to test the adsorption capacity of hydrotalcite.

These tests were all carried out using batch mode. Alternately, the experiments could be also be repeated using continuous systems to compare and identify which system is more effective.

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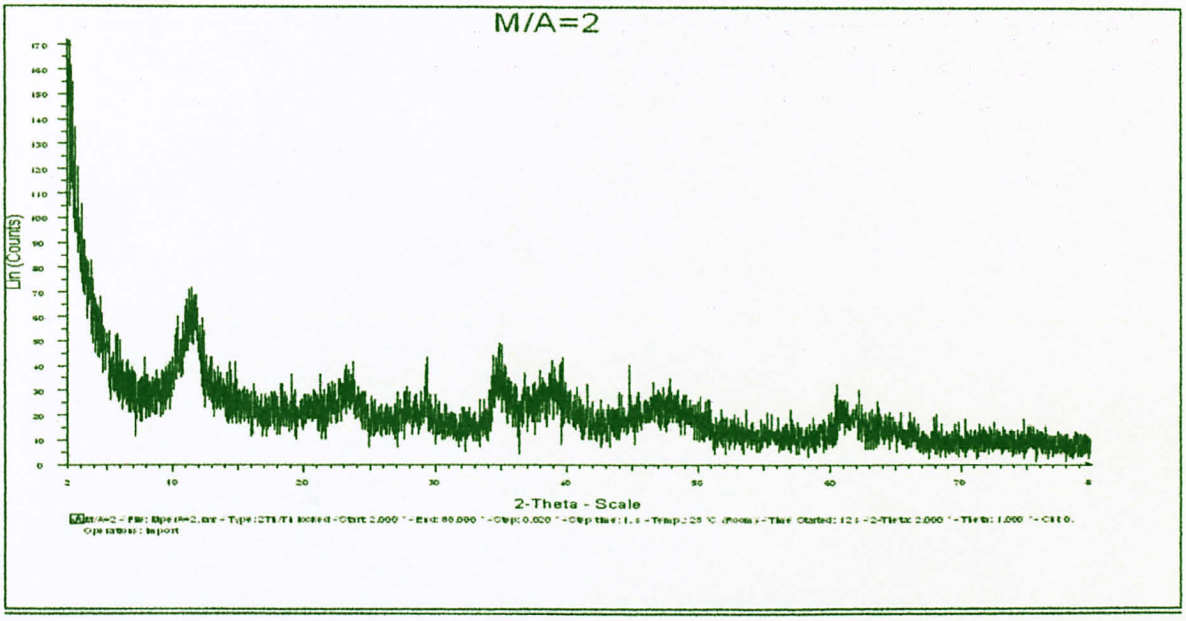
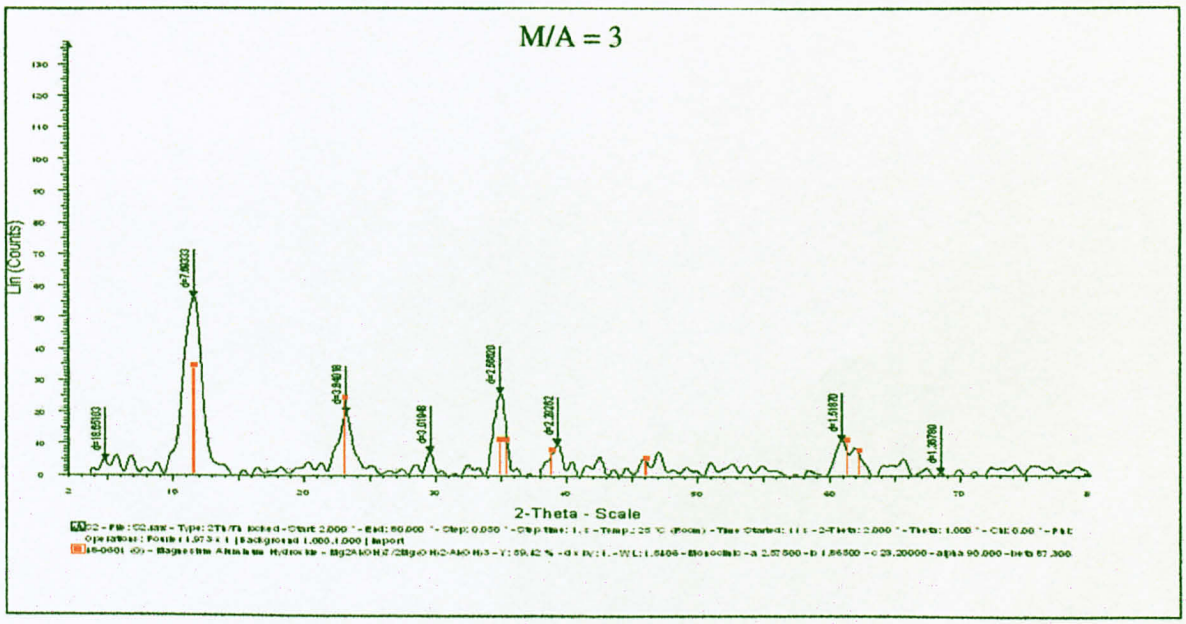
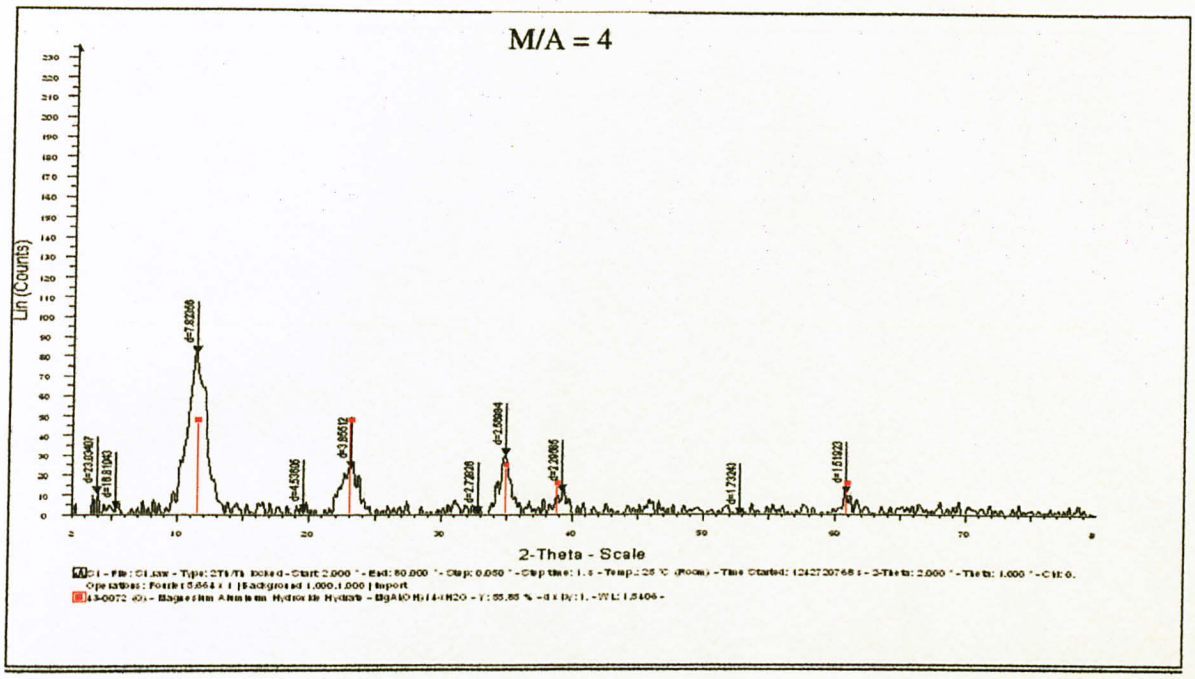
APPENDIX

XRD Results







Absorbance Value & Percentage of Adsorption

	time (hour)	50ppm	100ppm	150ppm
M/A = 2.0 m =0.4g	0	6.76	13.61	21.18
	0.08	6.56	11.12	20.93
	0.17	6.07	10.97	20.1
	0.33	5.96	10.41	18.47
	0.50	5.85	9.51	18.07
	0.75	4.81	8.61	15.01
	1.00	4.62	8.11	14.48
	1.25	3.91	7.55	13.52
	1.50	3.79	6.68	11.42
	1.75	3.62	5.24	10.25
	2.00	3.21	4.89	9.02
	2.25	2.71	4.27	7.69
	2.50	2.56	4.05	7.52
	2.75	2.38	3.5	6.34
	3.00	2.01	2.6	4.91
	3.25	1.79	2.23	4.5
	3.50	1.58	2.01	4.12
	3.75	1.32	1.89	3.74
	4.00	1.16	1.61	3.21
	8.00	1.12	1.51	3.07
	24.00	0.82	1.46	2.13

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	2.95858	18.29537	1.180359
0.17	10.2071	19.3975	5.09915
0.33	11.83432	23.51212	12.79509
0.50	13.46154	30.12491	14.68366
0.75	28.84615	36.73769	29.13126
1.00	31.6568	40.41146	31.63362
1.25	42.15976	44.52608	36.16619
1.50	43.93491	50.91844	46.08121
1.75	46.4497	61.4989	51.60529
2.00	52.51479	64.07054	57.41265
2.25	59.91124	68.62601	63.69216
2.50	62.13018	70.24247	64.49481
2.75	64.7929	74.28361	70.0661
3.00	70.26627	80.8964	76.81775
3.25	73.52071	83.61499	78.75354
3.50	76.62722	85.23145	80.54769
3.75	80.47337	86.11315	82.34183
4.00	82.84024	88.17046	84.84419
8.00	83.43195	88.90522	85.50519
24.00	87.86982	89.27259	89.94334

	time (hour)	50ppm	100ppm	150ppm
M/A = 2.0 m =0.2g	0	6.76	13.61	21.18
	0.08	6.56	12.89	20.73
	0.17	6.27	12.26	20.56
	0.33	5.96	11.67	18.87
	0.5	5.85	11.24	18.15
	0.75	5.43	10.89	17.43
	1	5.18	10.44	16.63
	1.25	4.96	10.08	15.89
	1.5	4.73	9.76	15.27
	1.75	4.48	9.43	14.38
	2	4.17	8.97	13.61
	2.25	3.94	8.54	13.11
	2.5	3.73	8.18	12.54
	2.75	3.48	7.63	11.92
	3	3.27	7.19	11.42
	3.25	3.06	6.67	10.83
	3.5	2.82	6.16	10.27
	3.75	2.68	5.74	9.76
	4	2.37	5.29	9.12
	8	1.81	3.31	5.32
	24	1.5	2.34	3.04

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	2.95858	5.290228	2.124646
0.17	7.248521	9.919177	2.92729
0.33	11.83432	14.25422	10.90652
0.5	13.46154	17.41367	14.30595
0.75	19.67456	19.9853	17.70538
1	23.37278	23.2917	21.48253
1.25	26.62722	25.93681	24.97639
1.5	30.02959	28.28802	27.90368
1.75	33.72781	30.71271	32.10576
2	38.31361	34.09258	35.74127
2.25	41.71598	37.25202	38.10198
2.5	44.82249	39.89713	40.7932
2.75	48.52071	43.93828	43.72049
3	51.62722	47.1712	46.08121
3.25	54.73373	50.99192	48.86686
3.5	58.28402	54.73916	51.51086
3.75	60.35503	57.82513	53.91879
4	64.94083	61.13152	56.94051
8	73.22485	75.67965	74.88196
24	77.81065	82.80676	85.64684

	time (hour)	50ppm	100ppm	150ppm
M/A = 3.0 m =0.2g	0	6.76	13.61	21.18
	0.08	6.36	12.77	20.75
	0.17	6.07	12.34	20.21
	0.33	5.76	11.84	19.34
	0.5	5.47	11.24	18.52
	0.75	5.18	10.94	17.33
	1	4.93	10.48	16.54
	1.25	4.62	9.87	15.68
	1.5	4.41	9.55	15.14
	1.75	4.13	9.02	14.26
	2	3.92	8.63	13.61
	2.25	3.75	8.21	13.04
	2.5	3.48	7.82	12.46
	2.75	3.15	7.35	11.63
	3	2.97	6.89	10.58
	3.25	2.69	6.45	9.92
	3.5	2.47	6.06	9.12
	3.75	2.21	5.65	8.63
	4	2.01	5.28	7.84
	8	1.6	3.45	4.27
	24	1.43	2.31	3.21

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	5.91716	6.171932	2.030217
0.17	10.2071	9.331374	4.579792
0.33	14.7929	13.00514	8.687441
0.5	19.08284	17.41367	12.55902
0.75	23.37278	19.61793	18.17753
1	27.07101	22.9978	21.90746
1.25	31.6568	27.47979	25.96789
1.5	34.76331	29.83101	28.51747
1.75	38.90533	33.7252	32.67233
2	42.01183	36.59074	35.74127
2.25	44.52663	39.67671	38.43248
2.5	48.52071	42.54225	41.17092
2.75	53.40237	45.99559	45.08971
3	56.06509	49.37546	50.04721
3.25	60.2071	52.60838	53.16336
3.5	63.46154	55.47392	56.94051
3.75	67.30769	58.48641	59.25401
4	70.26627	61.205	62.98395
8	76.33136	74.65099	79.83947
24	78.84615	83.02719	84.84419

M/A = 3.0
m =0.4g

time (hour)	50ppm	100ppm	150ppm
0	6.76	13.61	21.18
0.08	6.32	12.57	20.72
0.17	6.02	12.14	20.19
0.33	5.76	11.64	19.24
0.5	5.48	11.14	18.42
0.75	5.14	10.74	17.37
1	4.83	10.28	16.48
1.25	4.42	9.73	15.62
1.5	4.04	9.45	15.05
1.75	3.76	8.96	14.36
2	3.43	8.53	13.41
2.25	3.11	8.08	12.98
2.5	2.86	7.69	12.43
2.75	2.41	7.24	11.63
3	2.05	6.69	11
3.25	1.76	6.28	10.55
3.5	1.59	5.73	9.69
3.75	1.32	5.35	9.17
4	1.26	4.87	8.48
8	1.22	3.32	4.11
24	1.18	2.01	2.92

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	6.508876	7.64144	2.17186
0.17	10.94675	10.80088	4.674221
0.33	14.7929	14.47465	9.159585
0.5	18.93491	18.14842	13.03116
0.75	23.9645	21.08744	17.98867
1	28.5503	24.4673	22.19075
1.25	34.61538	28.50845	26.25118
1.5	40.23669	30.56576	28.9424
1.75	44.3787	34.16605	32.20019
2	49.26036	37.3255	36.68555
2.25	53.99408	40.63189	38.71577
2.5	57.69231	43.49743	41.31256
2.75	64.34911	46.80382	45.08971
3	69.67456	50.84497	48.06421
3.25	73.9645	53.85746	50.18886
3.5	76.47929	57.8986	54.24929
3.75	80.47337	60.69067	56.70444
4	81.36095	64.21749	59.96223
8	81.95266	75.60617	80.5949
24	82.54438	85.23145	86.21341

M/A = 2.0
m =0.6g

time (hour)	50ppm	100ppm	150ppm
0	6.76	13.61	21.18
0.08	6.47	11.02	20.72
0.17	6.02	10.87	19.87
0.33	5.92	10.21	18.37
0.5	5.79	9.43	17.26
0.75	4.72	8.55	16.1
1	4.54	8.1	14.23
1.25	3.87	7.47	13.12
1.5	3.71	6.48	11.12
1.75	3.52	5.18	10.18
2	3.21	4.72	8.95
2.25	2.68	4.19	7.69
2.5	2.46	3.99	7.22
2.75	2.28	3.32	6.12
3	1.96	2.52	4.52
3.25	1.65	2.13	4.35
3.5	1.44	1.98	4.03
3.75	1.25	1.79	3.52
4	1.12	1.53	3.06
8	0.97	1.31	2.34
24	0.75	1.27	1.82

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	4.289941	19.03012	2.17186
0.17	10.94675	20.13226	6.18508
0.33	12.42604	24.98163	13.26723
0.5	14.34911	30.71271	18.50803
0.75	30.17751	37.17855	23.98489
1	32.84024	40.48494	32.81398
1.25	42.75148	45.11389	38.05477
1.5	45.11834	52.38795	47.49764
1.75	47.92899	61.93975	51.93579
2	52.51479	65.31962	57.74315
2.25	60.35503	69.21381	63.69216
2.5	63.60947	70.68332	65.91124
2.75	66.27219	75.60617	71.10482
3	71.00592	81.4842	78.65911
3.25	75.59172	84.34974	79.46176
3.5	78.69822	85.45187	80.97262
3.75	81.50888	86.84791	83.38055
4	83.43195	88.75827	85.55241
8	85.65089	90.37472	88.95184
24	88.90533	90.66863	91.40699

	time (hour)	50ppm	100ppm	150ppm
M/A = 3.0 m =0.2g T = 50C	0	6.76	13.61	21.18
	0.08	6.24	12.65	20.64
	0.17	6.03	12.24	20.11
	0.33	5.73	11.72	19.28
	0.5	5.47	11.12	18.49
	0.75	5.14	10.72	17.3
	1	4.84	10.44	16.34
	1.25	4.53	9.63	15.66
	1.5	4.26	9.14	15.12
	1.75	4.03	8.48	14.23
	2	3.75	8.03	13.51
	2.25	3.42	7.64	12.88
	2.5	3.13	7.21	12.33
	2.75	2.86	6.51	11.63
	3	2.64	6.04	11
	3.25	2.28	5.47	10.58
	3.5	1.97	5.24	9.73
	3.75	1.65	4.72	9.33
	4	1.37	4.27	8.56
	8	1.21	3.13	4.23
	24	1.08	2.01	2.87

time (hour)	50ppm	100ppm	150ppm
0	0	0	0
0.08	7.692308	7.053637	2.549575
0.17	10.79882	10.06613	5.051936
0.33	15.23669	13.88685	8.970727
0.5	19.08284	18.29537	12.70066
0.75	23.9645	21.23439	18.31917
1	28.40237	23.2917	22.85175
1.25	32.98817	29.2432	26.06232
1.5	36.98225	32.8435	28.6119
1.75	40.38462	37.69287	32.81398
2	44.52663	40.99927	36.21341
2.25	49.40828	43.86481	39.18791
2.5	53.69822	47.02425	41.7847
2.75	57.69231	52.16752	45.08971
3	60.94675	55.62087	48.06421
3.25	66.27219	59.80896	50.04721
3.5	70.85799	61.4989	54.06043
3.75	75.59172	65.31962	55.94901
4	79.73373	68.62601	59.58451
8	82.10059	77.0022	80.02833
24	84.02367	85.23145	86.44948